

OPTICAL INSTRUMENT, AND
DEVICE MANUFACTURING METHOD

FIELD OF THE INVENTION AND RELATED ART

5 This invention relates to an optical
instrument and a device manufacturing method. More
particularly, the invention concerns an optical
instrument suitably usable in an exposure apparatus or
a spectroscope, for example, which uses light of a
10 wavelength in an ultraviolet region as a light source
and which has a function for preventing contamination
of an optical element provided therewithin. Also, the
invention concerns a device manufacturing method using
such optical instrument.

15 As regards light sources of optical
instruments, recently, shortening of the wavelength of
light has been required. Currently, in place of
standard ultraviolet rays, deep ultraviolet rays, X-
rays and EUV, for example, are used. Generally, the
20 shorter the wavelength is, the larger the optical
energy thereof is. For example, photon energies of
excimer lasers are 114.1 Kcal/mol (KrF excimer laser
of a wavelength 248 nm), 147.2 Kcal/mol (ArF excimer
laser of 193 nm), and 180.1 Kcal/mol (F₂ laser of 157
25 nm). As compared therewith, the binding and
dissociation energy of molecule is, for example, 84
Kcal/mol (C-C bond). Namely, photon energies in this

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wavelength region correspond to binding and dissociation energies of various substances. Thus, when a substance is irradiated with a photon energy, there occurs optical absorption or opto-chemical reaction.

On the basis of such property, light of such wavelength region can be used to process a substance. Also, because the optical characteristic such as absorption or reflection differs with a substance, it can be used for the structure analysis of a substance. Thus, light in such wavelength region is used in a lithographic process, a CVD process, and an etching process, and in various measurement instruments.

In such wavelength region, particularly, a wavelength region not longer than 220 nm, however, oxygen absorbs light. This is because, with the shortening of the wavelength, the photon energy becomes larger and there occurs light absorption by oxygen. In consideration of it, in optical instruments using light of such wavelength region, the light path of an optical system is kept at vacuum or is filled with an inactive gas to prevent absorption by oxygen. The absorption of light is caused not only by oxygen but also by various substances. Further, there may occur decomposition or composition of a substance by any opto-chemical reaction.

Therefore, a substance deposited on an

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optical element such as a lens, a mirror, a mask or a reticle, for example, may cause light absorption.

Also, a substance produced by an opto-chemical reaction may be deposited on an optical element and may cause deterioration of its optical characteristic.

In order to prevent such inconveniences, conventionally, an inactive gas to be supplied is kept at a high purity, or a filter for removing impurities (taking inorganic ion sulfate or ammonia as impurities) is mounted, for example.

Ammonium sulfate which is a typical contaminating substance is produced from sulfate ions and ammonium ions. The source of them may be those originally contained in an ambience gas of the optical instrument or those produced from the surface of a member. Further, it has been reported that, where water vapors are contained in a nitrogen gas ambience, irradiation of ultraviolet rays causes creation of ammonia. Also, it has been reported that an optical element may be contaminated by deposition of silicon oxide caused by an organic silicon compound.

The deterioration of optical characteristics of an optical element by deposition of a substance on its surface becomes more serious as the wavelength of a light source is shortened.

This is because, first, even if a substance deposited on an optical element does not adversely

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portions surrounding the optical elements, which may cause deposit contamination substances.

Therefore, not only the purity of a gas from a supply source but also matters decomposed from components of the optical instrument or a gas supply line, for example, should be considered from the standpoint of impurities, and it is necessary to design a contamination-free environment. The impurity production due to these factors is not constant. If there occurs deterioration of or defect in a component, the impurity concentration in the optical instrument will increase due to matters decomposed from the component, causing contamination of optical elements.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an optical instrument by which contamination of an optical element due to deposition of impurities can be reduced.

It is another object of the present invention to provide a device manufacturing method using such optical instrument.

There may be various impurities inside an optical instrument. Among them, particularly to those which may be deposited on an optical element to cause deterioration of its optical characteristic, the

density or concentration thereof should desirably be defined and the density inside the optical instrument should preferably be monitored and controlled. The impurity density in the ambience and the density of being deposited and accumulated on the surface of an optical element are at a certain proportion, for each substance, and are in a balanced state. Therefore, for suppressing deposition thereof on the surface of an optical element, it is necessary to decrease the impurity density or concentration in the ambience of the optical instrument and also to monitor and control the concentration.

In accordance with an aspect of the present invention, there is provided an optical instrument, comprising: an optical element; and a detector for detecting an impurity concentration in an ambience containing a space surrounding the optical element.

In accordance with another aspect of the present invention, there is provided an optical instrument, comprising: an optical element; a detector for detecting an impurity concentration in an ambience containing a space surrounding the optical element; and means for producing information of impurity concentration on the basis of an output of said detector.

In accordance with a further aspect of the present invention, there is provided an optical

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5 The optical instrument may be an exposure apparatus including (i) means for holding one of a mark and a reticle, (ii) an illumination optical system for illuminating a pattern of the mask or the reticle with the light, and (iii) means for holding a wafer to be exposed with the pattern. Also, the optical instrument may further comprise a projection optical system for projecting the pattern onto the wafer with use of the light, wherein said projection optical system is provided by (i) refractive elements only, (ii) reflective elements only, or (iii) a combination of refractive and reflective elements.

10 The detector may have a sensor for detecting a concentration of an organic substance.

15 The concentration of the organic substance may be controlled so that the total amount of organic substance in a gas inside said optical instrument becomes not greater than $1 \mu\text{g}/\text{m}^3$.

20 The concentration of the organic substance may be controlled so that each concentration of carboxylic acids, aldehydes, esters, phenols, phthalates, phthalic acids, amines, and amides is kept at $0.01 \mu\text{g}/\text{m}^3$ or less.

25 In accordance with a still further aspect of the present invention, there is provided a device manufacturing method, comprising the steps of: exposing a wafer with a device pattern by use of an

optical instrument as recited above; and developing the exposed wafer.

These and other objects, features and advantages of the present invention will become more apparent upon a consideration of the following description of the preferred embodiments of the present invention taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph for explaining the relationship between the total amount of organic substance as measured by GC/MS and deterioration of a transmission factor of quartz at 193 nm in one month.

Figure 2 is a schematic view of an arrangement including an optical element, in an embodiment wherein the present invention is applied to an exposure apparatus.

Figure 3 is a schematic view of an arrangement including a control unit, in an embodiment wherein the present invention is applied to an exposure apparatus.

Figure 4 is a schematic view of an arrangement in an embodiment wherein the present invention is applied to a spectroscopic system.

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In accordance with the present invention, substances which are present in an ambience and which may cause contamination of optical elements can be reduced as much as possible, so that deterioration of optical characteristics due to the contamination can be suppressed.

In an embodiment of the present invention, the impurity concentration in a gas is measured at a gas outlet port of an optical instrument. This enables monitoring the impurity concentration in the gas inside the optical instrument, while taking into account matters decomposed from components of the instrument. Further, the impurity concentration may be measured at a gas inlet port through which a gas is introduced into the optical instrument. By comparing the impurity concentrations at the gas outlet port and the gas inlet port with each other, the concentration of impurities produced inside the optical instrument can be detected. Since any local temperature inside the optical instrument or a gas flowing speed therein may apply an influence on the decomposition of impurities from a component thereof, local impurity concentration monitoring may preferably be made at one or plural locations inside the optical instrument. For example, in a high-temperature ambience, decomposition of a substance easily occurs from a

component and, therefore, the impurity concentration increases. Further, at a place where the gas flow is stagnant, the impurity concentration will increase. Therefore, it is desirable to monitor the impurity concentration at such places.

Where a sensor which is based on a non-dispersion infrared absorption method or a hydrogen flame ionization detection method, for example, is mounted, the impurity concentration in the gas can be monitored continuously while the optical instrument is kept in operation. Also, if it is sure that, at different locations inside the optical instrument, the impurity concentration in the gas changes small, the concentration measurement may be made periodically through GC/MS or the like. This enables stable operation of the optical instrument.

If the impurity concentration being monitored becomes higher than a predetermined level, in order to meet it, an output of a concentration sensor may be applied to a controller by which various controls may be done. An example of control is stopping the operation and adjusting the gas flow rate. Alternatively, a washing operation using an opto-chemical reaction or ozones may be made, to decrease the impurity concentration.

Next, the results of measurement made to changes in transmission factor of a quartz placed in

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an environment, in relation to an embodiment of the present invention, will be described.

5 The concentration of organic substances in the environment was measured by using a GC/MS heating desorption method. Figure 1 shows the relation between the organic substance concentration (toluene conversion) in the ambience as measured by the GC/MS heating desorption method and the degree of deterioration of the transmission factor of the quartz with respect to light of a wavelength 193 nm.

10 If the organic substance concentration is high, there occurs substance deposition on the quartz surface, and it causes contamination thereof and decreases the transmission factor. However, where the quartz is kept in an environment wherein the organic substance concentration is decreased, the transmission factor decrease is suppressed. Further, depending on each substances and in accordance with their vapor pressures and polarities, attraction of them to the surface is different. A quartz was placed in an environment ambience and organic substances in the environment as well as organic substances deposited on the surface of the quartz were measured on the basis of the GC/MS heating desorption method. The results showed that there were different tendencies in detected organic substances. While many hydrocarbons were present in the environment ambience, on the other

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hand there were much carboxylic acids and phthalates deposited on the quartz surface, more than hydrocarbons.

Thus, carboxylic acids, aldehydes, esters, phenols, phthalates, phthalic acids, amines, and amides, for example, have functional groups with a high polarity such as carboxyl group, aldehyde group, ester group, phenyl group, and amino group, for example, and they are easily deposited on the surface of an optical element. When concentrations of these substances in the environment ambience were held low, deterioration of the optical characteristic was suppressed.

Thus, it has been confirmed that, in order to prevent deterioration of the optical characteristic of optical elements in an optical instrument, the organic substance concentration inside the instrument should be adjusted as follows.

Namely, the total amount of organic substances is held not greater than $1 \mu\text{g}/\text{m}^3$, and carboxylic acids, aldehydes, esters, phenols, phthalates, phthalic acids, amines, and amides should be kept at $0.01 \mu\text{g}/\text{m}^3$ or less.

When this is done, deterioration of optical characteristic of an optical element due to contamination thereof can be prevented or suppressed effectively.

In relation to all gas-purged spaces including an optical element in a projection exposure apparatus (e.g., the inside space of a barrel of an illumination optical system or the inside space of a barrel of a projection optical system), the impurity concentration may be measured. Figure 2 shows a general structure. As for the purging, a clean dry air or an inactive gas such as N_2 gas or He gas, for example, may be used. As regards components used in a gas supply unit and in the exposure apparatus, those materials causing smallest degassing are selected. Also, if necessary, a filter or the like is mounted. The organic substance (impurity) concentration is monitored by means of sensors 7a and 7b. These sensors may be of the type based on the non-dispersion infrared absorption method or the hydrogen flame ionization detection method, for example, and they are operable to perform continuous measurement. The sensors 7a are mounted at gas inlet ports 3, and the sensors 7b are mounted at gas outlet ports 5. From differences in the concentrations detected by them, the impurity concentration produced inside the instrument can be detected continuously.

As described above, by providing plural sensors at different locations inside the optical

instrument and by comparing the detected impurity concentrations while taking into account the flows of gases, flowing through the instrument, a particular place, if any, where the impurity concentration becomes higher can be specified.

The impurity concentration measurement may be made periodically in accordance with the GC/MS measurement.

Figure 3 illustrates a general structure including an impurity concentration controlling function. The impurity concentration as measured by a sensor means 13 (13a and 13b) is outputted to a controller 11. In the controller 11, the measured concentration is compared with a predetermined value. If the measured concentration becomes higher than the predetermined value, the controller 11 applies a control signal to relevant units. The operation of a light source 8 may be stopped, which is effective to prevent deposition of substances on the surface of an optical element such as a lens, a mirror, a reticle or a mask, as produced by an opto-chemical reaction of causal matters, i.e., impurities in the gas.

If the impurity concentration measured by the sensor 13a at the gas inlet port side becomes higher than that measured by the sensor 13b at the gas outlet port side, it means that the gas 4 being supplied or a gas supply unit supplying the gas involves its cause.

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If the impurity concentration measured by the sensor 13b at the gas outlet port side is higher than that measured by the sensor 13a at the gas inlet port side, it means that the cause for increase of impurity concentration is involved in the optical system unit 12 of the instrument. If the impurity production is temporary, such impurities will be discharged by continuously flowing the gases 4 and 6. Thus, after it is confirmed through a controller 14 that the impurity concentration as outputted from the sensor 13b becomes lower than the predetermined level, the operation of the light source 11 may be re-started. This is convenient in that, by increasing the gas flow rate flowing through the instrument, the impurity concentration is effectively decreased and that the operation of the instrument can be re-started promptly.

An ozone generator 16 may be provided to supply ozones into the optical system unit 12, including optical elements, to wash the optical elements. Alternatively, oxygens may be injected into the optical instrument and light may be projected thereto, by which ozones or activated oxygens may be produced to wash the optical elements therewith. As a washing method, an opto-chemical reaction method may

be used wherein light may be projected to the whole inside space of the instrument or wherein an optical catalyst may be used.

5 As regards the washing process, where sensors are mounted at different locations inside the instrument, the washing process may be performed by the controller 14 only at such location where the concentration becomes higher than the predetermined level.

10 With the gas flow rate adjustment or the washing process performed by a predetermined time period, the impurity concentration can be decreased. Once it is confirmed through the controller 14 that the impurity concentration as measured by the sensor means 13 is decreased below the predetermined level, the operation of the light source 11 is re-started.

15 Figure 4 shows a general structure in an embodiment wherein the present invention is applied to a spectroscope system. Gases are flown through various portions inside the system, and sensors 28 (28a and 28b) are mounted to monitor the impurity concentration. The sensor means 28 outputs the impurity concentration in the gas. If the measured concentration becomes higher than a predetermined value, a controller 29 stops a light source and performs the gas flow rate adjustment as well as a washing process using ozones, for example. In this

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manner, contamination of optical elements inside the system as well as a measurement sample therein is prevented.

A few examples will now be described.

[Example 1]

A quartz parallel plate of a size 30 mm diameter and 3.0 mm thickness was stored in a conventional environment (total organic substance amount of a few tens $\mu\text{g}/\text{m}^3$), being supplied with a N_2 gas. After it was stored therein by one month, the transmission factor with respect to 193 nm, for example, was decreased by about 0.3%. The substances deposited on the surface of the quartz plate having been stored were analyzed by the GC/MS heating desorption method. The results showed that phthalates such as DBP, for example, phenols such as BHT, for example, carboxylic acids such as palmitic acid, for example, as well as amines and ethers were detected.

In consideration of the above, from the environment including the N_2 gas line, plastic materials used in phthalates such as DBP or DOP as a plastic agent as well as plastic materials using BHT as an anti-oxidation agent were removed. The concentration each of carboxylic acids, aldehydes, esters, phenols, phthalates, phthalic acids, amines, and amides was kept at $0.01 \mu\text{g}/\text{m}^3$ or less, and the

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total organic substance amount was kept at $1 \mu\text{g}/\text{m}^3$ or less. After a quartz plate was kept in such environment for one month, there was no change in transmission factor thereof. Also, according to the analysis based on the GC/MS heating desorption method, no deposition was found on the surface thereof. Thus, deposition of organic substances on the quartz and contamination thereby were prevented effectively.

[Example 2]

Like the quartz plate, a fluorite was examined. In a conventional storage method, the transmission factor with respect to 193 nm was decreased in one month by about 0.3%. As regards surface deposited matters, phthalates and carboxylic acids as well as aldehydes were detected. Where organic substances in a storage environment were controlled in accordance with the conditions set by the present invention, no deterioration of the transmission factor was found. Further, no surface deposition was detected. Thus, satisfactory results were obtained also in regard to fluorite.

[Example 3]

Similar examinations were made to a sample having an anti-reflection coating formed thereon. In a conventional storage method, deterioration of

transmission factor was observed. Also, surface depositions were detected. Under the conditions set by the present invention, the transmission factor was kept constant, and no deposition was detected.

5 It was confirmed that, as long as the organic substance amount was not greater than a predetermined value, circulation of N_2 gas through the inside space of the instrument had a sufficient effect to maintain the optical characteristic of an optical element
10 therein.

While the invention has been described with reference to the structures disclosed herein, it is not confined to the details set forth and this application is intended to cover such modifications or
15 changes as may come within the purposes of the improvements or the scope of the following claims.

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